

merization or hydrogenation, we conclude than an initial Fe-C<sub>2</sub>H<sub>4</sub> matrix is required for these reactions to occur. When finely divided iron powder is generated by the sodium amalgam reduction of FeCl<sub>2</sub> in THF in the presence of ethylene, no dimerization or hydrogenation of the ethylene is observed.

### Experimental Section

**Starting Materials.** Ethylene, propenes, and the butenes were used as received from Matheson Gas products. The iron used was iron filings (degreased) from Matheson Coleman and Bell and was heated above its melting point (1808 K) under high vacuum for 3 min prior to evaporation. Ethylene-d<sub>4</sub> was purchased from Merck and Co. Deuterium oxide was obtained from Stohler Isotope Chemicals. Gas Chromatographic analyses of hydrocarbon products were carried out on a 20-ft dimethylsulfolane column with a Carle micro detector. Infrared measurements were carried out on a Perkin-Elmer Model 983 spectrometer. <sup>1</sup>H nuclear magnetic resonance spectra were measured on a Bruker 400 MHz spectrometer while <sup>13</sup>C spectra were run on a Nicolet 300-MHz instrument. Gas chromatography-mass spectrometry was carried out with a Dupont 491b spectrometer interfaced with a Varian 2700 GC and Finnigan data system.

**General Procedure for the Reaction of Iron Atoms with Ethylene.** The metal atom reactor is based on that described by Timms<sup>15</sup> in which Fe atoms are evaporated from a resistively heated molybdenum alumina crucible under high vacuum and deposited on the walls of a 2-L flask at 77 K. The crucibles are prepared by coating a spiral of 50-mil Mo wire (H. Cross Co.) with an aqueous suspension of alundum cement (Fischer), drying successively at 473 K and 973 K, and finally by passing a current of 55 A through the Mo wire under vacuum. In a typical experiment, 3-18 mmol of Fe are evaporated over a 30-min period and cocondensed with 10 mmol of C<sub>2</sub>H<sub>4</sub>. If an additional substrate is to be added, it is distilled into the reactor after cocondensation of iron and ethylene. The reactor is allowed to warm to room temperature and stand for 1 h. The volatile products are pumped from the reactor through traps at 133 K and 77 K. The 77 K trap contains mainly recovered ethylene and ethane which is quantitated by IR spectroscopy. The 133 K trap contains the remaining hydrocarbons which are identified by IR spectroscopy and mass spectrometry and quantitated by GC.

**Analysis of Deuterated Products.** A statistical mixture of the deuterated and protiated ethylenes was prepared by the procedure of Paul<sup>16</sup> which involved the reduction of a 1:2:1 mixture of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>HD, and C<sub>2</sub>D<sub>2</sub> with Cr<sup>2+</sup> in 1:1 H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub>. The IR spectrum of this mixture was similar to that obtained from cocondensation of Fe with 1:1 C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub>. When D<sub>2</sub>O was added to the Fe-C<sub>2</sub>H<sub>4</sub> matrix, C<sub>2</sub>H<sub>3</sub>D was identified in the recovered ethylene by its IR band at 809 cm<sup>-1</sup>.<sup>17</sup> No other deuterated ethylenes could be detected in the IR. The deuterium content of the propene recovered from the Fe-C<sub>2</sub>D<sub>4</sub> matrix was evaluated from its 400-MHz <sup>1</sup>H NMR spectrum.

**Reduction of Ferrous Chloride in the Presence of Ethylene.** Ferrous chloride (0.5 g, 4.3 mmol) and naphthalene (0.2 g, 1.5 mmol) were dissolved in 50 mL of dry THF. The solution was frozen at 77 K and degassed, and 1% Na(Hg) (0.5 g, 21 mmol of Na) was added. This mixture was then allowed to warm in the presence of 10 mmol of ethylene with stirring. The production of finely divided Fe powder was complete within 5 min of warming. The mixture was allowed to stir for an additional 1 h and the ethylene was analyzed in the usual manner. No ethane or C<sub>4</sub> hydrocarbons were detected.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are grateful to Drs. William T. Evanochko and Charles Watkins for running the high-field NMR spectra. We thank

Mr. Gitendra C. Paul for the preparation of the statistical mixture of protiated and deuterated ethylenes.

**Registry No.** Fe, 7439-89-6; C<sub>2</sub>H<sub>4</sub>, 74-85-1; H<sub>2</sub>, 1333-74-0; C<sub>2</sub>D<sub>4</sub>, 683-73-8; D<sub>2</sub>O, 7789-20-0; (Z)-2-butene, 590-18-1; ethane, 74-84-0; butane, 106-97-8; 1-butene, 106-98-9; ethylene-d<sub>1</sub>, 2680-00-4; ferrous chloride, 7758-94-3; naphthalene, 91-20-3; (E)-2-butene, 624-64-6.

### Molybdenum Atom Desulfurizations of Organosulfur Compounds

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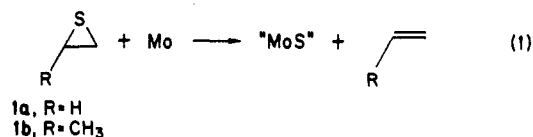
Received May 4, 1984

Molybdenum and its compounds are important constituents of a large number of desulfurization and hydrodesulfurization catalysts which are finding increasing utility in the removal of sulfur from fuels and their combustion products.<sup>2</sup> In order to investigate the initial interaction between molybdenum and sulfur in such processes, we have studied the reaction of a number of simple organosulfur compounds with atomic Mo.<sup>3</sup>

Since the molybdenum-sulfur bond is quite strong, it was anticipated that the use of highly energetic ( $\Delta H_f = 659$  kJ/mol),<sup>4</sup> sterically nondemanding, and coordinatively unsaturated Mo atoms should effect the removal of sulfur from organosulfur compounds in a clean and straightforward manner. To a large extent these expectations were realized in that several organosulfur compounds gave sulfur-free hydrocarbon products. Not surprisingly, the efficiency of desulfurization was found to be critically dependent on the strength of the carbon-sulfur bond.

### Results and Discussion

The reactions of Mo atoms with both cyclic and acyclic organosulfur compounds were carried out by cocondensing atomic Mo with the organic substrate at 77 K, allowing the mixture to warm to room temperature and analyzing volatile products. In the case of small-ring heterocycles, the expectation that relief of ring strain would lead to facile desulfurization was realized. Thus, when Mo atoms were cocondensed with thiirane, **1a**, and 2-methylthiirane, **1b**, the corresponding alkenes were generated in 132% and 119% yield, respectively, based on Mo vaporized, as shown in eq 1. In this and all cases, the molybdenum and sulfur



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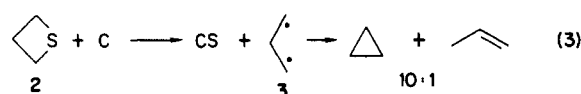
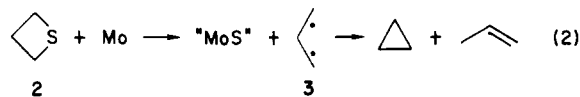
**Table I. Yields of Volatile Products from the Reaction of Molybdenum Vapor with 2-Methylthiirane, Thietane, 1-Propanethiol, and Diallyl Sulfide**

product	yield from <sup>1b</sup> 2-methylthiirane, %	yield from thietane, %	yield from 1-propanethiol, %	yield from diallyl sulfide, %
propylene	119	45.2	8.7	123
cyclopropane	0	3.6	0	0
ethylene	0	1.4	17.6	0
propane	0	1.7	47.1	1.1

<sup>a</sup> Yields based on molybdenum vaporized. In all cases a large excess of organosulfur compound is employed.

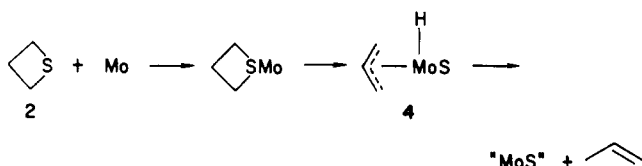
remained in the reactor as a nonvolatile residue. Although the presence of excess metal hampered elemental analysis of these residues, they were shown to consist primarily of molybdenum and sulfur with very little carbon and hydrogen. An examination of the IR spectrum of these nonvolatile residues revealed a peak at 390 cm<sup>-1</sup> which we attribute to MoS<sub>2</sub>. The spectrum (Nujol mull) of MoS<sub>2</sub> also shows a peak at 390 cm<sup>-1</sup>.<sup>5</sup>

The cocondensation of molybdenum vapor with thietane, **2**, a four-membered ring system, also leads to desulfurization with the production of mainly propene and cyclopropane as shown in Table I. While it is tempting to speculate that this desulfurization proceeds via the simultaneous cleavage of two carbon-sulfur bonds to generate the trimethylene biradical, **3** (eq 2), systems in



which **3** is known to be an intermediate generally produce higher ratios of cyclopropane to propene than is observed here. Thus, the reaction of atomic carbon with **2**, postulated to proceed via **3** (eq 3), gives a ratio of cyclopropane:propene of 10:1.<sup>6</sup> The ratio of cyclopropane to propene obtained in the reaction of Mo vapor with **2** is 1:12, indicating that the biradical pathway is not followed in this reaction.

As an alternative to the direct formation of **3** it is proposed that the reaction proceeds via a ( $\pi$ -allyl)molybdenum hydride intermediate, **4**. Subsequent decomposition of



**4** upon warming generates propene and a molybdenum sulfide phase. The loss of propene from ( $\pi$ -allyl)molybdenum hydride complexes containing phosphine ligands has been reported by Byrne, Blaser, and Osborn.<sup>7</sup>

Attempts to trap intermediate **4** have been unsuccessful. The addition of tetraethylthiuram disulfide to the matrix prior to warming does not result in the formation of the known Mo(S<sub>2</sub>CNEt)<sub>4</sub>,<sup>8</sup> but does increase the propene yield from 45% to 77%. It seems reasonable to assume that the

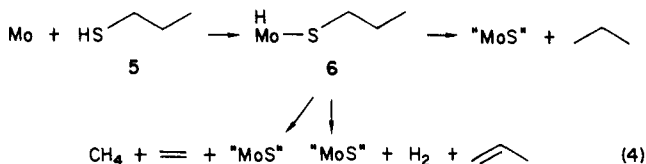
**Table II. Yields of Volatile Products from the Reaction of Molybdenum Vapor with 1-Butanethiol and Tetrahydrothiophene**

product	yield from 1-butanethiol, %	yield from tetrahydrothiophene, %
hydrogen	16.3	17.8
methane	0	0.9
ethane	2.2	2.9
ethylene	1.6	3.4
propane	trace	1.5
propene	trace	0.6
butane	9.3	0.8
1-butene	0	trace
1-butanethiol		15.5
thiophene	<i>b</i>	2.4

<sup>a</sup> Based on molybdenum vaporized. <sup>b</sup> Not analyzed.

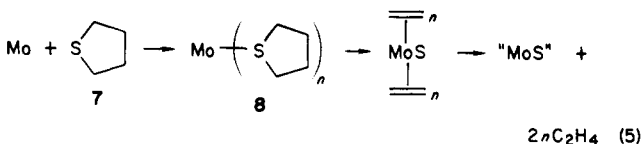
disulfide assists in the displacement of the propene from a polymeric MoS phase.

Table I demonstrates that desulfurization of 1-propanethiol, **5**, also occurs upon reaction with Mo vapor. In this case, the major product is propane indicating that reductive desulfurization of **5** occurs. We postulate that an initial insertion by a Mo atom into a sulfur-hydrogen bond of **5** generates a (propanethiolato)molybdenum hydride, **6** which subsequently eliminates propane. Intermediate **6** may also give rise to the observed ethylene and propene as shown in eq 4. The other anticipated frag-



mentation products, hydrogen and methane (eq 4), were not analyzed as they are not trappable at 77 K. The cocondensation of Mo and 1-butanethiol gives similar products, although in lower yields, as shown in Table II.

Table II also demonstrates that reaction of Mo vapor with tetrahydrothiophene, **7**, is a complex process in which desulfurization represents only a minor pathway. The main reaction is the formation of hydrogen and considerable amounts of reduction products. By analogy with the mechanism proposed for the reaction between Mo and **2**, we postulate that **7** reacts with Mo to generate an initial tetrahydrothiophene complex **8**. This complex, which may be similar to a tetrahydrothiophene-solvated Mo atom, can then undergo C-S insertion leading ultimately to desulfurization with the formation of ethylene shown in eq 5.



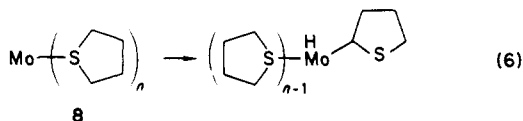
Alternately, complex **8** can undergo a C-H insertion by Mo to generate a molybdenum hydride as shown in eq 6. This hydride then serves as an intra- and intermolecular

(5) Crystalline samples and pressed pellets of MoS<sub>2</sub> show absorption at ca. 384 cm<sup>-1</sup>. Cf. Wieting, T. J.; Verble, J. L. *Phys. Rev. B* 1971, 3, 4286. Garg, A. K. *Phys. Status Solidi B* 1976, 76, 171.

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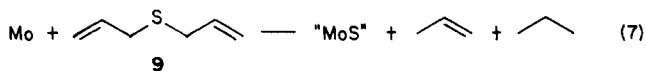


reducing agent which initiates the formation of the reduced products. We have previously reported the reduction of olefinic double bonds with similar hydrido intermediates formed by the cocondensation of Mo vapor with tetrahydrofuran.<sup>9</sup>

The fact that no cyclobutane is generated in the desulfurization of **7** provides evidence that the tetramethylene biradical is not involved. Cocondensation of carbon atoms with **7** gives a 9:1 ratio of ethylene to cyclobutane in a reaction that is thought to involve the intermediacy of the tetramethylene biradical.<sup>6</sup> The addition of carbon monoxide to the matrix of Mo and **7** at 77 K does not result in the trapping of the known<sup>10</sup> tris(tetrahydrothiophene)molybdenum tricarbonyl.

It is obvious that the decreasing reactivity toward desulfurization by Mo atoms as one proceeds from a three- to a four- to a five-membered heterocycle is a result of the decrease in ring strain. Tetrahydrothiophene, in which the C-S bonds are not appreciably weakened by this effect, shows little desulfurization with initial C-H insertion predominating.

In order to assess the effect of C-S bond strength on the ease of desulfurization by Mo atoms, we have cocondensed Mo with diallyl sulfide, **9**. In this molecule, the allylic C-S bond is weaker than the aliphatic C-S bond in **7** by roughly 60 kJ/mol.<sup>11</sup> This decrease in C-S bond strength manifests itself in a facile desulfurization which generates propene in 123% yield along with a small amount of propane (eq 7).



These experiments demonstrate that organosulfur compounds are reactive toward Mo atoms at low temperatures. Those molecules with weak C-S bonds appear to undergo exclusive desulfurization while those containing C-S bonds of normal strength undergo C-H insertion and reduction more readily than desulfurization. Although the removal of sulfur from compounds such as **1** and **2** has no practical utility, these systems may serve as a model for the initial interaction between a reactive molybdenum center and an organic sulfur of the type that occurs in high temperature desulfurizations. It is anticipated that these reactions, which take advantage of the high exothermicity of metal-sulfur bond formation, may occur with other metals which can form strong M-S bonds such as W, Pt, Ca, Ta, and Ni.

### Experimental Section

The cocondensation reactions were carried out in a metal atom reactor similar to that described by Skell and co-workers.<sup>12</sup> A sample of molybdenum wire (2.5–4.0 g) was bent into a "U" shape and bolted to the two water-cooled brass electrodes. A current of 60–70 A was used to vaporize molybdenum. Reactions were carried out on the walls of the reactor at ca. 77 K with the internal pressure of the reactor being kept below 10<sup>-4</sup> torr to preclude gas-phase reactions between molybdenum atoms and substrate

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molecules. 2-Methylthiirane was synthesized by the method of Snyder, Stewart, and Ziegler.<sup>13</sup> The other organosulfur compounds were commercial samples and were used as received. All samples were outgassed by three freeze-pump-thaw cycles prior to their introduction into the vacuum system. Upon completion of a given cocondensation, the reactor was closed to the vacuum system and allowed to warm to ambient temperatures under static vacuum. Volatiles were subsequently removed by vacuum distillation through a series of slush baths at various temperatures.

Infrared spectra were recorded on Perkin-Elmer 337, 580, and 621 spectrophotometers. Gas chromatography was performed on a Carle 100 gas chromatograph or, in the case of gas chromatography-mass spectrometry, on a Varian Aerograph 2700 interfaced to a DuPont 491-B mass spectrometer outfitted with a Finnegan INCOS data system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Cocondensation of Molybdenum Vapor with Thiirane.** Mo vapor (0.530 mmol) was cocondensed with thiirane (3.0 mL, 51.8 mmol) over a 30-min period. A yellowish red matrix formed which turned brown prior to melting. Pumpout and analysis of volatiles gave ethylene (0.700 mmol) as the sole gaseous product.

**Cocondensation of Molybdenum Vapor with 2-Methylthiirane.** Mo vapor (0.772 mmole) was cocondensed with 2-methylthiirane (10.0 mL, 149.0 mmol) over a 30-min period to give an orange matrix which turned brown-red upon melting. Pumpout and analysis of volatiles gave propene (0.920 mmol) as the sole gaseous product.

**Cocondensation of Molybdenum Vapor with Thietane.** Mo vapor (0.661 mmol) was condensed with thietane (10.0 mL, 135 mmol) over a 30-min period to yield a bright yellow matrix which turned brown upon melting. Pumpout and analysis of volatiles gave propene (0.299 mmol), cyclopropane (0.023 mmol), ethylene (0.001 mmol), and acetylene (trace).

**Cocondensation of Mo Atoms with 1-Propanethiol.** Mo vapor (0.367 mmol) was cocondensed with 1-propanethiol (15 mL, 166 mmol) over a 20-min period to yield a reddish yellow matrix which turned brown on warming to room temperature under static vacuum. Analysis of volatile products showed propane (0.163 mmol) as the major product, along with propene (0.025 mmol), ethylene (0.065 mmol), and acetylene (8.13 × 10<sup>-4</sup> mmol).

**Cocondensation of Mo Atoms with Butanethiol.** Mo (0.410 mmol) was cocondensed with 10 mL (94 mmol) of butanethiol over a 20-min period to yield a yellow matrix which turned brown upon warming to room temperature under static vacuum. Analysis of volatiles showed hydrogen (6.68 × 10<sup>-2</sup> mmol), ethane (9.02 × 10<sup>-3</sup> mmol), propene (trace), ethylene (6.65 × 10<sup>-3</sup> mmol), and butane (3.81 × 10<sup>-2</sup> mmol). No methane or 1-butene was detected.

**Cocondensation of Mo Atoms with Tetrahydrothiophene.** Mo (0.540 mmol) was cocondensed with 23 mL (26 mmol) of tetrahydrothiophene over a 30-min period to yield a yellow matrix which turned brown on warming to room temperature under static vacuum. Analysis of volatile products showed butanethiol (8.1 × 10<sup>-2</sup> mmol), 1-butene (trace), butane (4.23 × 10<sup>-3</sup> mmol), propylene (3.24 × 10<sup>-3</sup> mmol), propane (8.1 × 10<sup>-3</sup> mmol), ethylene (1.84 × 10<sup>-2</sup> mmol), methane (4.86 × 10<sup>-3</sup> mmol), hydrogen (9.61 × 10<sup>-2</sup> mol), and thiophene (1.29 × 10<sup>-2</sup> mmol).

**Reaction of Molybdenum Vapor with Allyl Sulfide.** Molybdenum vapor (2.31 mmol) was cocondensed with 10 mL (78 mmol) of allyl sulfide over a 20-min period, a brilliant orange-yellow matrix forming during codeposition. Upon completion the reactor was sealed from the pumps and allowed to come to room temperature. Volatiles were pumped out through -78 °C and -196 °C traps. Analysis of the -196 °C fraction gave propene (2.850 mmol) and propane (0.0243 mmol) as sole volatile products.

**Acknowledgment.** Partial support of this work through an Auburn University Energy Research Grain-in-Aid is gratefully acknowledged. The technical assistance of Mr. Eugene Nelson is deeply appreciated.

**Registry No.** **1a**, 420-12-2; **1b**, 1072-43-1; **2**, 287-27-4; **5**, 107-03-9; **7**, 110-01-0; **9**, 592-88-1; butanethiol, 109-79-5; molybdenum, 7439-98-7.

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